On the Interplay between Swelling Kinetics and Nanostructure in PFSA Thin-films: Role of Hygrothermal Ageing

Meron Tesfaye [†, ‡], Douglas I. Kushner [‡], Ahmet Kusoglu [‡, *]

[†] Chemical and Biomolecular Engineering, University of California Berkeley, Berkeley, CA, 94720

[‡] Energy Storage & Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720

[*]Author to whom correspondence should be addressed: akusoglu@lbl.gov

Abstract

Impacts of processing, storage, and operation on thin-film perflurosulfonic-acid (PFSA) ionomer coatings used in electrodes of electrochemical devices remains unestablished. In this work, alteration of structure-function relationship in ionomers is achieved via exposure to elevated temperature and humidity (hygrothermal ageing). Findings reflect a strong inverse correlation between ageing-induced ionomer thin-film domain orientation and water-transport kinetics evaluated from swelling. Impact of ageing is shown to be more pronounced on platinum, due to interactions with PFSA, as evidenced by greater increase in nano-domain orientation parallel to substrate accompanied by reduced water transport, in contrast to silicon support.

Keywords:

ionomer thin-films, hygrothermal ageing, nanostructure, domain orientation, time constant, water transport kinetics

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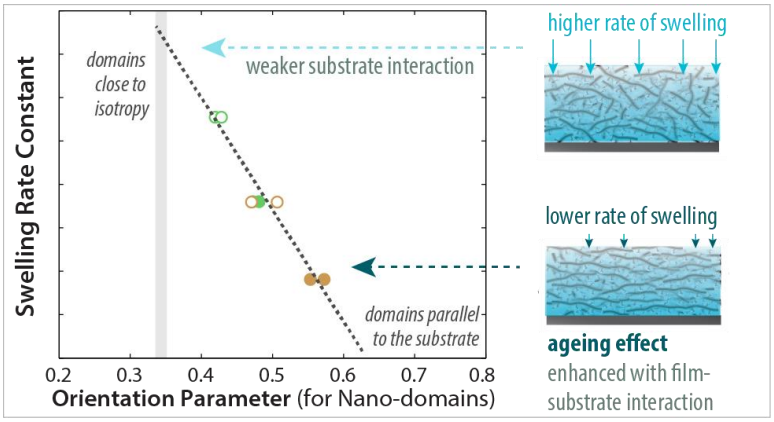

Perfluorosulfonic-acid (PFSA) ionomers serve as benchmark polymer electrolytes for various clean-water and energy-conversion electrochemical technologies.[1] Integral to its ion- and water-transport capabilities is PFSA's phase-separated structure, which is enhanced upon hydration of its -SO_3H end groups and maintained by the mechanical stability of its inert backbone matrix.[1] As a random copolymer lacking well-defined structure, comprehension of PFSA's intrinsic structure-function relationship has heavily dependent on processing conditions (i.e. pre-treatment, cation contamination, *etc*.), thermal history (unmanned, annealed, hot-pressed, *etc*.), and external stimuli (i.e. humidity, solvent, *etc*.).[1,2] However, engineering high-performance ionomers requires establishment of fundamental relationship between morphology of PFSA and properties that dictate performance.[2] This is even more consequential for PFSA thin-films (nanometers in thickness), as local interfaces and interactions impose additional constraints that limit critical properties, impeding electrode performance in energy-conversion devices.[3,4] Various examples of confinement-driven limitations in thin-film ionomers include decreased water uptake, diffusivity, ion conductivity, accompanied by an overall increase in transport resistance and mechanical stiffness.[1,3–7] While these property changes have been ascribed to substrate-dependent morphological changes, interfacial interactions, and finite-size driven enthalpic and entropic strains, few have resulted in definitive predictive correlations.[5,8] To that effect, this study aims to explicitly correlate substrate-dependent morphology (nano-structural orientation) with water-sorption kinetics (swelling property) by employing hygrothermal ageing.

While some environmental conditions intrinsic to device operation (such as hydration) are necessary to maintain PFSA functionality, they can also permanently alter

structure and functionality over time.[9–11] Notably, prolonged exposure of bulk PFSA to hot and humid conditions (hygrothermal ageing) results in dramatic changes in ionomer properties, altering ionomer's morphology, increasing mechanical properties and reducing water uptake and conductivity.[9–13] Although no such explorations on the impact of ageing in PFSA thin-films exists thus far, the technique of prolonged solvent exposure and different processing conditions are frequently employed in block-copolymer thin-films to access different morphologies.[14–16] In supported ionomer thin-films, similar to ionomers present in electrodes, morphological changes cannot be decoupled from supporting substrates. Recent findings have reported ionomer thin-film swelling property depends on the chemical composition of substrates (platinum/oxidized platinum (Pt/PtO_x), gold (Au), and carbon (C)), which may even be dictated during film formation, highlighting the key role substrate interactions play in controlling film behavior.[3,7,17] Thin-films exhibit phase-separated domains under humidification, similar to a membrane, but with anisotropy driven by substrate and confinement effects.[3,18] While thin-films on silicon substrates with native oxide (Si/SiO_x) exhibits close to isotropic patterns (random domain orientation), films on hydrophobized Si or metallic substrates exhibit anisotropic domain orientation, which is further enhanced for film thicknesses <50 nm.[1,3] This work demonstrates a direct link between ionomer thin-film swelling, which serves as proxy for ion conductivity and water transport, to substrate dependent nano-structural orientation as accessed by hygrothermal ageing.

In this study, 30-40nm thin-films of PFSA with long- and medium-side-chain length (Nafion and 3M respectively) were spun-cast on Si/SiO_x and Pt/PtO_x substrates to mimic ionomers in electrochemical electrodes. The films were then hygrothermally aged for 2-4

days in an environmental chamber held at 85% relative humidity (RH) and a temperature of 70 °C. Structural changes caused by hygrothermal ageing are investigated via *in-situ* grazing incidence small-angle X-ray scattering (GISAXS). Fig. 1 summarizes the GISAXS patterns of unaged (as-cast) and aged PFSA thin-films on Si/SiO_x and Pt/PtO_x support. An ionomer peak (at q_{peak} = 2 to 2.5 nm^{-1}) is apparent in all, and more pronounced in aged thin-films (Fig. 1a), signifying the phase-separated nanostructure with a correlation length of d = $2\pi/q_{peak}$ = 2.5 to 3 nm. Upon hydration, the ionomer peak shifts to lower q (large d) due to incorporation of water molecules into hydrophilic nano-domains. Interestingly, changes in peak position as well as peak shape upon hydration are less distinct for aged films where the hydrophilic-domain network appears to already be expanded and set as a result of ageing.[3,18] (See SI for further discussion). The high-intensity regions around the specular peak in the GISAXS images (Fig. 1a) highlight the hygrothermal ageing-induced anisotropic structure. To analyze structural anisotropy, the intensity distributions around the ionomer peak position (q_{peak} = 2.5 ± 0.25 nm^{-1}) are taken from the 2D GISAXS spectra and plotted as a function of azimuthal angle, $I(\chi)$ (Fig. 1b). Films on the Si/SiO_x substrate exhibit a low degree of anisotropy and closely follow the ideal isotropic distribution ($I(\chi)$ = constant). Hygrothermally-aged thin-films prepared on Pt/PtO_x exhibit an intensity distribution, concentrated at q_p = 0, which indicates more domains are orientated parallel to the surface. A domain orientation parameter, *O.P.*, quantifies the anisotropy of such distributions:[3]

$$O.P. = \left\langle \cos^2 \chi \right\rangle = \frac{\int_0^{\pi/2} I(\chi)\sin(\chi)\cos^2 \chi d\chi}{\int_0^{\pi/2} I(\chi)\sin(\chi)d\chi} \langle S \rangle_{domain} = \frac{1}{2}\langle 3\omega_{ori}\text{-}1 \rangle \quad [1]$$

where *O.P.* is between 0 (domains perpendicular to the substrate) and 1 (domains parallel to the substrate) and is 0.33 for an isotropic structure (random domain orientation). Fig. 1c shows the *O.P.* for PFSA thin-films increases upon hygrothermal ageing. In addition, there is a higher *O.P.* for aged long side-chain PFSA (Nafion over 3M), revealing the possible role of pendant chain chemistry in these governing interactions.[18] Fig. 1c shows increased nanostructural orientation on Pt/PtO_x compared to Si/SiO_x, in both as-cast (unaged) and aged state. Aged thin-films on Pt/PtO_x, also showed greater *O.P.* distribution probably due to the dynamic interactions between water and Pt/ionomer interface.[3,17,19,20]

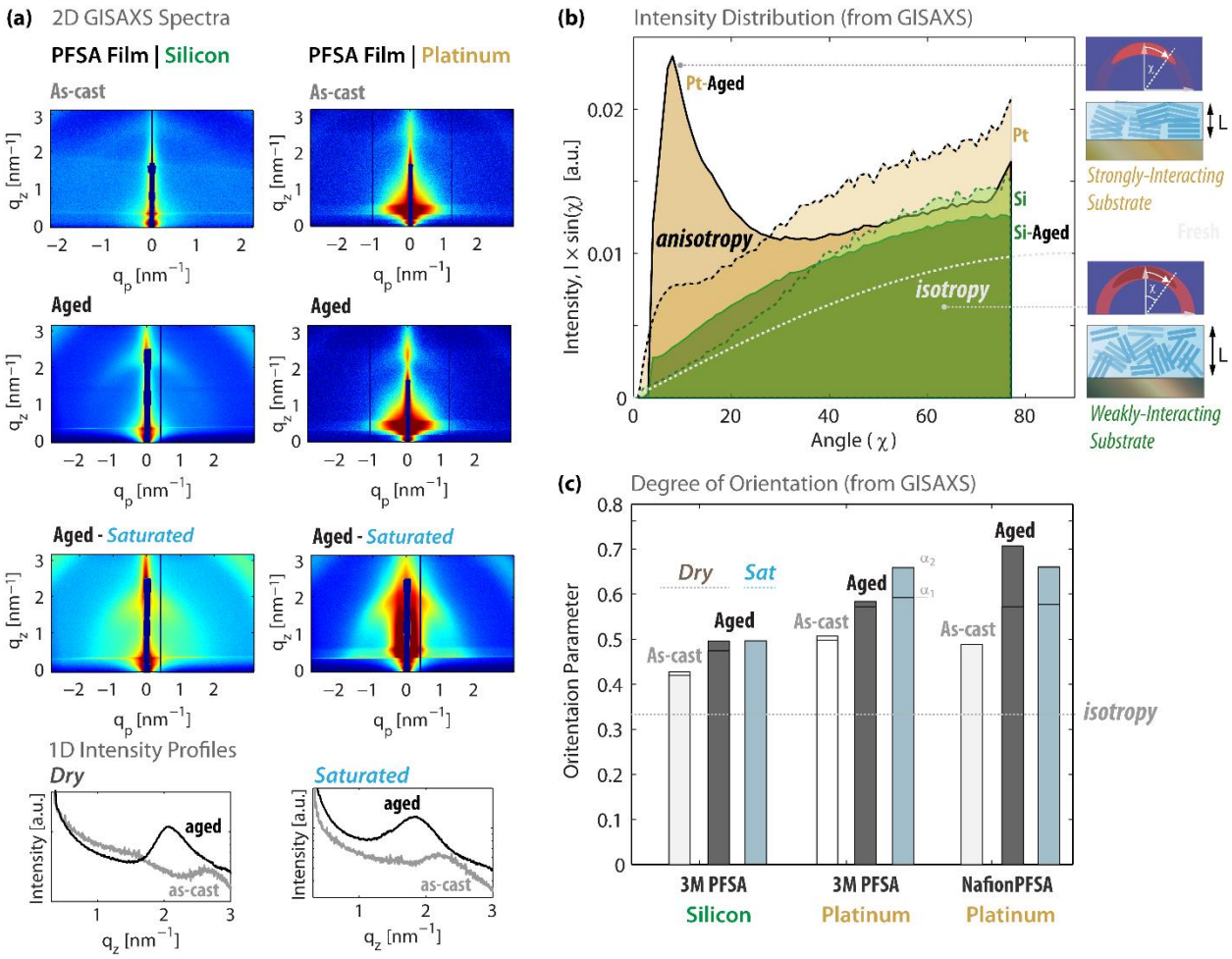

Figure 1: (a) 2D GISAXS images of as-cast (unaged) and hygrothermally aged PFSA (3M, 825g/mol equivalent weight) thin-films spin-cast on Si/SiO_x and Pt/PtO_x substrate in dry (33%) and saturated (100% RH) conditions at 26 ºC. 1D intensity profiles are shown below for the 3M PFSA films on Si/SiO_x substrate, based on the 2D images. (b) Intensity distribution as a function of azimuthal angle, χ, for the ionomer peak. The solid and dashed lines represent the aged and as-cast samples, respectively, and the dotted line shows the distribution calculated for an ideal isotropic case. (c) Orientation parameter calculated from the distributions in (b). The low and high bars correspond to low and high incidence angle. (See SI for details).

The effect of hygrothermal ageing on ionomer swelling extent and kinetics was captured by *in-situ* spectroscopic ellipsometry. Fig. 2 compares swelling of aged and as-cast PFSA ionomer thin-films on Si/SiO_x and Pt/PtO_x substrates at 97% RH. In contrast to hygrothermally-aged films coated on Si/SiO_x, which show a 12% reduction in swelling, aged films on Pt/PtO_x exhibit a 50% reduction in extent of swelling normal to the substrate. For comparison, the same water-uptake reduction from reference (unaged) bulk PFSAs

(~50 μm thick) would require 100 days of hygrothermal ageing;[21] this difference between bulk and thin-film aging highlights the enhanced interplay of confinement and substrate on thin-film PFSAs. The effect of ageing is amplified on strongly-interacting substrates like Pt/PtO_x,[3,17,19,22] which accelerates the ageing process.

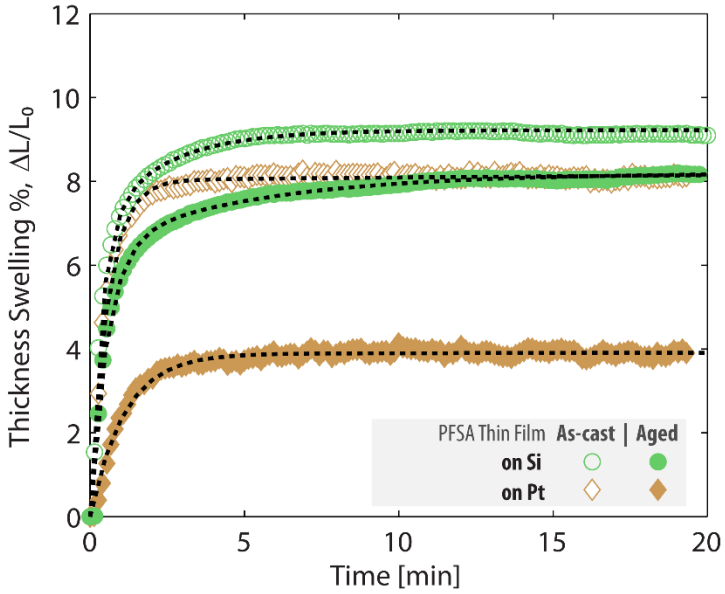

Figure 2: Time-dependent fractional thickness swelling of PFSA (3M) thin-films (nominal thickness, $L_0 \approx 34$ nm) spin cast on Si/SiO_x and Pt/PtO_x substrates during humidification from 0 to 97 % RH. Data are shown for as-cast (unaged) and aged (at 85% RH, 70 °C for 4 days) films. The dashed lines are best-fit to the measured data (symbols) using a two-term exponential expression, discussed later.

To quantify this explicitly, ageing-induced changes in thin-film nanostructure (Fig. 1) can be correlated with water-sorption dynamics by investigating swelling kinetics (Fig. 2). The time-dependent swelling process is analyzed by fitting the normalized transient thickness change (Fig. 2) to a two-term exponential expression[1]:

$$\frac{L(t)-L_0}{L_\infty-L_0} = 1 - \mathrm{A}\exp\left(-\frac{t}{\tau_1}\right) - (1-\mathrm{A})\exp\left(-\frac{t}{\tau_2}\right) \quad [2]$$

where τ_1 and τ_2 are time constants for the short-term (fast, diffusional transport) and long-term (slow, physical relaxation and interfacial transport) swelling processes,

respectively.[1,23] Fig. 3a shows the inverse time constant of water sorption kinetics, $k_s = 1/\tau$, against *O.P.* Assuming one-dimensional swelling in thin-films, interfacial transport and water diffusion can be estimated from characteristic time constants τ_2 ($=L/k_{int}$) and τ_1 ($=L^2/D_{water}$), respectively. D_{water} in ionomer thin-films explored here ranges from 10^{-12} cm^2/s to 10^{-13} cm^2/s; reduction in D_{water} tracks with increasing *O.P.* and is on the same order of magnitude as those reported by Eastman *et. al.*[24] Unaged films on Pt/PtO_x possess strong orientation and ageing increases structural parallel orientation on both supports, presumably impacting through-plane water transport. Considering the primary governing water transport mechanism to be interfacial transport, $k_{int} = L/\tau_2$ (ranging from 10^{-6} to 10^{-8} cm/s) illustrates a different aspect of ageing. Change in *O.P.* is strongly coupled with diffusional transport, which is accompanied by swelling at early times, while interfacial relaxation becomes dominant at longer time-scales ($\tau_1 > \tau_2$) and is dependent on *O.P.* to a lesser extent. For comparable ageing-induced change in *O.P.*, thin-films on Pt/PtO_x show higher time constant relative to Si/SiO_x, perhaps due to differences in substrate/ionomer interaction compounded by physical ageing (relaxation) that has been shown to be accelerated on metal supports.[20,22,25] However, the key takeaway is ageing-induced morphological rearrangement (*O.P.*) is inversely correlated to characteristic rate for swelling (k_s) representing water transport kinetics (or time constant is proportional to *O.P.*, i.e., $\tau \propto 1/k_s \propto O.P.$).

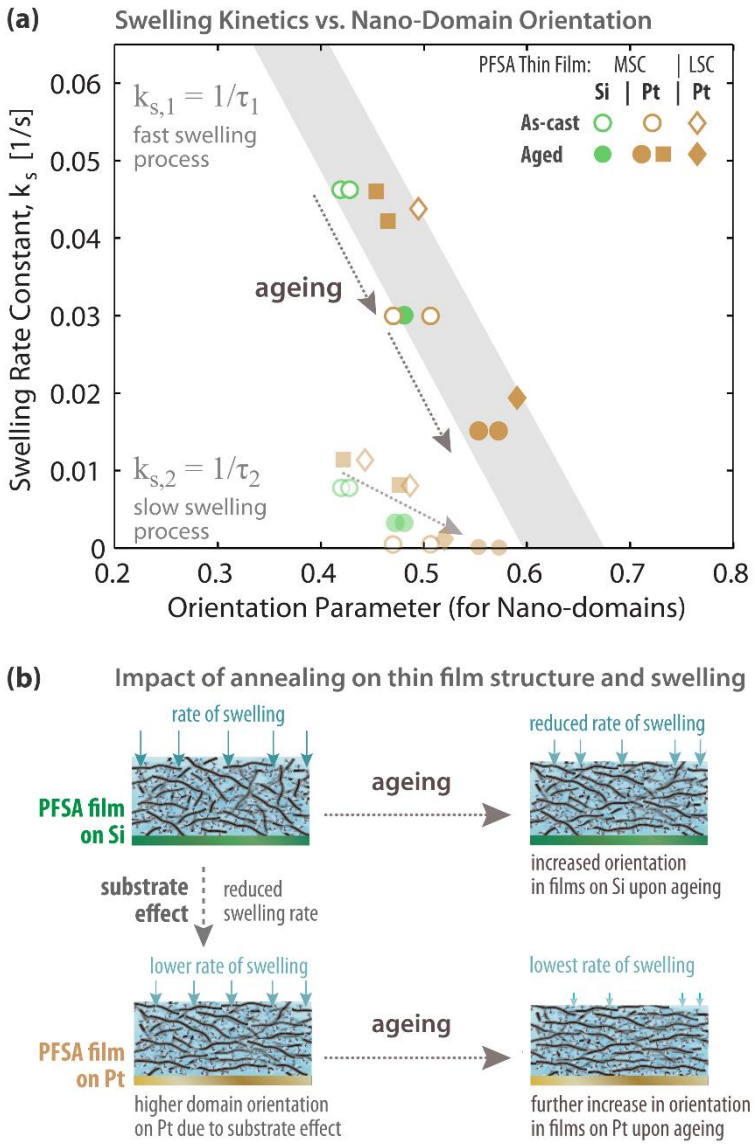

Figure 3: (a) Swelling rate constants of as-cast (unaged) and aged 3M (■,●) and Nafion (♦) PFSA thin-films during humidification to saturation (from ellipsometry) plotted against the orientation parameter of the same film in dry condition (from GISAXS). All the films were annealed after casting, except the unannealed 3M film on Pt (■), which is shown for comparison. Two rate constants are plotted for each case, representing the fast and slow swelling processes. (From Eq. (2)). (b) The schematics illustrate the inverse relationship between increasing domain orientation (parallel to the interfaces) and kinetics of swelling. The shaded region is shown as the guide for-the-eye.

Ionomer hydration controls transport properties like ion conduction and gas diffusion. Tunable nanostructures that control hydration and transport pathways can be designed via synthesis or processing techniques for well-ordered ionomers like sulfonated block or graft copolymers.[2] A similar attempt is made here via hygrothermal ageing of disordered thin-film PFSAs, whose properties are subject to additional surface interaction effects that are heightened with finite size. Previous studies have demonstrated that alignment of hydrophilic moieties at the ionomer surface, governed by the interactions of the ionomer with vapor or liquid,[3,26–28] is related to mass-transport of water.[1,26,28] Findings in this work reflect similar stimulus(hygrothermal ageing)-driven, surface(Pt/PtO_x)-controlled, and chemistry (side-chain) influenced preferential orientation resulting in water transport limitations in ionomer thin-films. A number of postulations are made here to explain this direct correlation and reduction in ionomer water transport/swelling rate with increase in *O.P.*:

(1) Increasing backbone alignment parallel to the substrate selectively lowers through-plane water transport by lowering hydrophilic surface area and increasing tortuosity, similar to the effect of structurally-induced orientation on ion transport.[7,8] Ageing-induced chain orientation increases the fraction of $-SO_3^-$ moieties near the substrate, intensifies their pairwise interactions, which could further enhance orientation, and reduces swelling and swelling kinetics perpendicular to the substrate.

(2) Coupled with previous postulate on kinetics, hygrothermal ageing induces order in the nanostructure, enabling the ionomer to access different quasi-equilibrium states.[29] This is in similar vein to processing induced alignments in di-block polymers.[2,16,30] Such a structure could preserve substrate/film interactions that

perpetuate and stabilize the chain configurations that could alter swelling governed by thermodynamic equilibrium. Comparative ageing and morphological studies in other solvents could elucidate the role of solvent and reversibility in achieving alternative structures to decouple the kinetic and thermodynamic effects.

(3) Distinct from the other two possible explanations is sulfonic anhydride formation, similar to that occurring in bulk PFSA.[9,10,21] Anhydride formation increases equivalent weight via physical crosslinking of ionomer chains and reduces water uptake. This explanation would imply that enhanced order and interaction on Pt/PtO_x accelerates anhydride formation in ionomer over Si/SiO_x support. Spectroscopic studies on aged thin-films could provide insight into presence of other forms of degradation and anhydride formation.

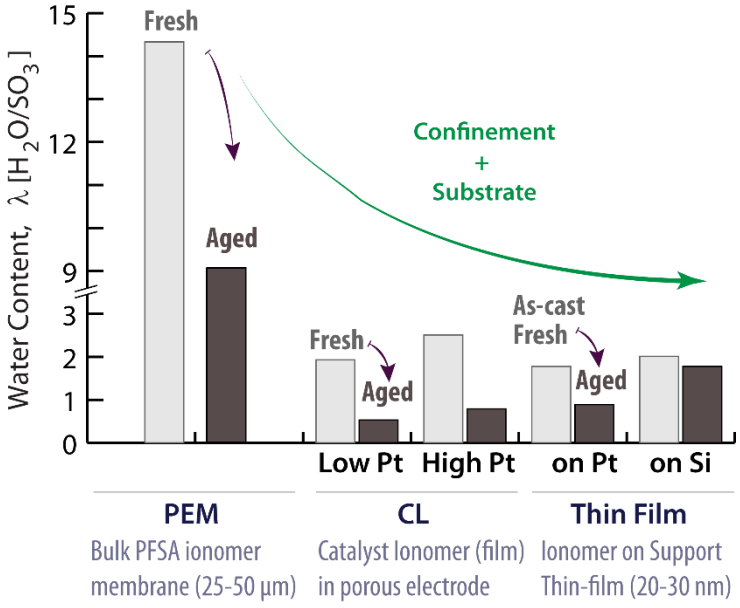

Figure 4: Comparison of maximum ionomer water content (at 95-97%RH) in bulk membrane,[10] catalyst layer (CL), and thin-films on a support (PFSA for PEM is Nafion, while for CL and thin-films 3M PFSA is used. See SI for full description of materials and treatment conditions).

These results on thin-film swelling are consistent with our hydration measurements on the unaged and aged catalyst layers (CLs) of varying Pt loading (see SI); higher Pt loading reflects significant reduction in water uptake with hygrothermal ageing compared to low-loaded CL (Fig. 4). Thus, findings herein shed light into the ionomer structure-related origins of the performance limitations in fuel-cell electrodes that may occur during operation, and how they might be influenced by the dynamic substrate-ionomer interactions. It must be noted that correlating ionomer's structure-swelling changes to performance is not trivial due to variations in the Pt/ionomer interface such as surface roughness (Figure S2 in Supporting Information) and substrate composition along with environmental effects (reducing or oxidizing), which were shown to consequently alter thin-film swelling.[17]

This letter reports compelling evidence for the existence of an explicit correlation between the orientation of nano-domains and swelling kinetics in PFSA ionomer thin-films, which is evidenced by ageing-induced changes in the film's nanostructure and swelling. The higher the orientation parallel to film surface, the slower the transport normal to surface. Stronger interactions between ionomer side-chains and Pt/PtO_x enhances the impact of hygrothermal ageing by preferentially aligning more of the backbone parallel to the substrate. Domain alignment and re-alignment caused by environment (e.g., hygrothermal ageing and saturation) and ionomer/substrate interactions dictates swelling behavior and water transport in thin-films. Notably, the temperature used in this study for ageing is much less than the initial annealing temperatures (70 ºC vs. 140-160 ºC), which underscores the role of water as an important stressor driving the film towards structural reorganization that influence material properties. Results presented herein provide new

insights into the impact of environmental conditioning on inducing morphological changes in ionomer thin-films, a phenomenon of great importance for elucidating and controlling their structure/function relationship and transport response at dynamic interfaces in energy conversion devices.

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Supporting Information:

Associated Content: Full experimental methods are provided in detail in Supporting Information.

Reference

(1) Kusoglu, A.; Weber, A. Z. New Insights into Perfluorinated Sulfonic-Acid Ionomers. *Chem. Rev.* **2017**, *117*, 987–1104.

(2) Park, M. J.; Hong, J.; Kim, S. Y. Role of Nanostructures in Polymer Electrolytes for Energy Storage and Delivery. In *ACS Symposium Series 1096; Polymers for Energy Storage and Delivery: Polyelectrolytes for Batteries and Fuel Cells*; 2012; pp 129–146.

(3) Kusoglu, A. Ionomer Thin Films in PEM Fuel Cells. In *Encyclopedia of Sustainability Science and Technology*; Meyers, R., Ed.; Springer, New York, NY, 2018.

(4) Kongkanand, A.; Gu, W.; Mathias, M. F. Proton-Exchange Membrane Fuel Cells with Low-Pt Content. In *Encyclopedia of Sustainability Science and Technology*; 2018.

(5) Tesfaye, M.; Kushner, D. I.; McCloskey, B. D.; Weber, A. Z.; Kusoglu, A. Thermal Transitions in Perfluorosulfonated Ionomer Thin-Films. *ACS Macro Lett.* **2018**, 1237–1242.

(6) DeCaluwe, S. C.; Baker, A. M.; Bhargava, P.; Fischer, J. E.; Dura, J. A. Structure-Property Relationships at Nafion Thin-Film Interfaces: Thickness Effects on Hydration and Anisotropic Ion Transport. *Nano Energy* **2018**, *46*, 91–100.

(7) Ono, Y.; Nagao, Y. Interfacial Structure and Proton Conductivity of Nafion at the Pt-Deposited Surface. *Langmuir* **2016**, *32*, 352–358.

(8) Nagao, Y. Proton-Conductivity Enhancement in Polymer Thin Films. *Langmuir* **2017**, *33*, 12547–12558.

(9) Naudy, S.; Collette, F.; Thominette, F.; Gebel, G.; Espuche, E. Influence of Hygrothermal

Aging on the Gas and Water Transport Properties of Nafions Membranes. *J. Memb. Sci.* **2014**, *451*, 293–304.

(10) Shi, S.; Dursch, T. J.; Blake, C.; Mukundan, R.; Borup, R. L.; Weber, A. Z.; Kusoglu, A. Impact of Hygrothermal Aging on Structure/Function Relationship of Perfluorosulfonic-Acid Membrane. *J. Polym. Sci. Part B Polym. Phys.* **2016**, *54*, 570–581.

(11) Shi, S.; Chen, G.; Wang, Z.; Chen, X. Mechanical Properties of Nafion 212 Proton Exchange Membrane Subjected to Hygrothermal Aging. *J. Power Sources* **2013**, *238*, 318–323.

(12) Onishi, L. M.; Prausnitz, J. M.; Newman, J. Water - Nafion Equilibria. Absence of Schroeder's Paradox. **2007**, 10166–10173.

(13) Hensley, J. E.; Way, J. D.; Dec, S. F.; Abney, K. D. The Effects of Thermal Annealing on Commercial Nafion Membranes. *J. Memb. Sci.* **2007**, *298*, 190–201.

(14) Stewart-Sloan, C. R.; Olsen, B. D. Protonation-Induced Microphase Separation in Thin Films of a Polyelectrolyte-Hydrophilic Diblock Copolymer. *ACS Macro Lett.* **2014**, *3*, 410–414.

(15) Gu, X.; Gunkel, I.; Hexemer, A.; Russell, T. P. Controlling Domain Spacing and Grain Size in Cylindrical Block Copolymer Thin Films by Means of Thermal and Solvent Vapor Annealing. *Macromolecules* **2016**, *49*, 3373–3381.

(16) Sinturel, C.; Vayer, M.; Morris, M.; Hillmyer, M. A. Solvent Vapor Annealing of Block Polymer Thin Films. *Macromolecules* **2013**, *46*, 5399–5415.

(17) Tesfaye, M.; MacDonald, A. N.; Dudenas, P. J.; Kusoglu, A.; Weber, A. Z. Exploring

Substrate/Ionomer Interaction under Oxidizing and Reducing Environments. *Electrochem. commun.* **2018**, *87*, 86–90.

(18) Kusoglu, A.; Dursch, T. J.; Weber, A. Z. Nanostructure/Swelling Relationships of Bulk and Thin-Film PFSA Ionomers. *Adv. Funct. Mater.* **2016**, *26*, 4961–4975.

(19) Yagi, I.; Inokuma, K.; Kimijima, K.; Notsu, H. Molecular Structure of Buried Perfluorosulfonated Ionomer/Pt Interface Probed by Vibrational Sum Frequency Generation Spectroscopy. *J. Phys. Chem. C* **2014**, *118*, 26182–26190.

(20) Kodama, K.; Motobayashi, K.; Shinohara, A.; Hasegawa, N.; Kudo, K.; Jinnouchi, R.; Osawa, M.; Morimoto, Y. Effect of the Side-Chain Structure of Perfluoro-Sulfonic Acid Ionomers on the Oxygen Reduction Reaction on the Surface of Pt. *ACS Catal.* **2018**, *8*, 694–700.

(21) Collette, F. M.; Lorentz, C.; Gebel, G.; Thominette, F. Hygrothermal Aging of Nafion. *J. Memb. Sci.* **2009**, *330*, 21–29.

(22) Selvan, M. E.; He, Q.; Calvo-Munoz, E. M.; Keffer, D. J. Molecular Dynamic Simulations of the Effect on the Hydration of Nafion in the Presence of a Platinum Nanoparticle. *J. Phys. Chem. C* **2012**, *116*, 12890–12899.

(23) Kongkanand, A. Interfacial Water Transport Measurements in Nafion Thin Films Using a Quartz-Crystal Microbalance. *J. Phys. Chem. C* **2011**, *115*, 11318–11325.

(24) Eastman, S. A.; Kim, S.; Page, K. A.; Rowe, B. W.; Kang, S.; Soles, C. L.; Yager, K. G. Effect of Confinement on Structure, Water Solubility, and Water Transport in Nafion Thin Films. *Macromolecules* **2012**, *45*, 7920–7930.

(25) Kushner, D. I.; Hickner, M. A. Substrate-Dependent Physical Aging of Confined Nafion Thin Films. *ACS Macro Lett.* **2018**, *7*, 223–227.

(26) Novitski, D.; Holdcroft, S. Determination of O2 Mass Transport at the Pt | PFSA Ionomer Interface under Reduced Relative Humidity. *ACS Appl. Mater. Interfaces* **2015**, *7*, 27314–27323.

(27) Hwang, G. S.; Parkinson, D. Y.; Kusoglu, A.; Macdowell, A. A.; Weber, A. Z. Understanding Water Uptake and Transport in Nafion Using X-ray Microtomography. *ACS Macro Lett.* **2013**, *2*, 288–291.

(28) He, Q.; Kusoglu, A.; Lucas, I. T.; Clark, K.; Weber, A. Z.; Kostecki, R. Correlating Humidity-Dependent Ionically Conductive Surface Area with Transport Phenomena in Proton-Exchange Membranes. *J. Phys. Chem. B* **2011**, *115*, 11650–11657.

(29) Kim, T. H.; Yi, J. Y.; Jung, C. Y.; Jeong, E.; Yi, S. C. Solvent Effect on the Nafion Agglomerate Morphology in the Catalyst Layer of the Proton Exchange Membrane Fuel Cells. *Int. J. Hydrogen Energy* **2017**, *42*, 478–485.

(30) Kim, J.; Kim, B.; Jung, B.; Kang, Y. S.; Ha, H. Y.; Oh, I. H.; Ihn, K. J. Effect of Casting Solvent on Morphology and Physical Properties of Partially Sulfonated Polystyrene-Block-Poly(Ethylene-Ran-Butylene)-Block-Polystyrene Copolymers. *Macromol. Rapid Commun.* **2002**, *23*, 753–756.